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CONTEMPORARY SOVIET METHODS
OF AUTOMATIC GAS ANALYSIS IN INDUSTRY

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Figures are appended.

Automatic methods of gas analysis are becoming more and more important every year. This is connected with the fact that laboratory methods in many cases do not meet the requirements of continuous production control, and that they are completely unsuitable in those cases where automatic regulation of the production process is indicated by the composition of the gas.

Until recently, a great portion of the problems of automatic gas analysis in industry were solved by means of volumetric gas analyzers and gas analyzers based on the measurement of heat conductivity. For many years, these initial designs formed the basis of technological gas analysis.

New problems in gas analysis could not be solved by these methods and designs. The process of development of the technology of automatic analysis amounts, in principle, to the replacement of mechanized chemical analysis methods and intermittent tests by continuous analyses based on physicochemical and physical principles.

The specific features of capitalist economy are reflected in the development of automatic analysis technology abroad.

Above all, one must bear in mind the competition which requires the appearance of many modifications of apparatus which are identical in their design features, but for the development of which there is no real technical basis.

It must also be considered that there are patent limitations which, in a number of cases, have led to the output of technically unjustified designs to circumvent the patents of a competitor.

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The firms concerned, for instance, tried to revive interest in chemical automatic gas analysis. This resulted in unsuccessful attempts to increase the accuracy of analysis in the Mono-Micro and Ados gas analyzers equipped with water thermostats, the entire scale of which comprised, for example, 0-1 percent in the case of oxygen. Analogous attempts to increase the accuracy of analysis by reducing the effect of friction in the apparatus, at the cost of introducing a complicated movement, were carried out in the Thermotekhnika gas analyzer. Characteristically, in one of the latest models of the Monoduplex gas analyzer, a signal appliance for incomplete combustion products (CO and H₂) has been built which is based on the change in resistance of a platinum coil on which the combustible gases are burned. In other words, the indicator of a periodically acting electric gas analyzer was built into a chemical gas analyzer. This kind of combination is pointless, technically speaking, and unwarranted. In addition to these attempts, the creation of automatic manometric gas analyzers was also carried out; these are distinguished by the fact that instead of the usual measurement of decrease of volume, they measure the rarefaction caused by the absorption of the component being analyzed. This does, indeed, increase the sensitivity of the apparatus, but it introduces a number of complications which are not justified by the technical effect achieved by this method.

In the article below, some present-day questions of automatic gas analysis and recently developed methods for their solution are discussed.

Determination of Oxygen

Automatic determination of oxygen in gas mixtures is of special importance among problems of gas analysis. Of particularly great importance is the determination of the oxygen content in industrial furnaces, boiler combustion chambers, and internal-combustion engines.

Many metallurgical and chemical processes must be controlled and regulated as regards the oxygen content, particularly those carried out with the use of air enriched in oxygen.

There are still a number of cases requiring control of the oxygen content, such as the determination of small quantities of oxygen in combustible gases. This is of great importance from the viewpoint of explosion prevention.

Usually, the value of the coefficient of excess air is determined by an analysis for carbon dioxide, sometimes with the additional determination of the products of incomplete combustion.

Oxygen control has a number of essential advantages:

1. For determining the coefficient of air excess with the same accuracy, the permissible error in O₂ analyzers is three times as great as the error in CO₂ analyzers. [1]
2. In the control of a process with incomplete combustion, the indication of the CO₂ analyzer is not conclusive. Thus, in bituminous coal combustion chambers, 16 percent CO₂ may stand for a +15 percent air excess or a -10 percent air deficiency. With the indicated air excess, the O₂ content would be 3.5 and 0 percent, respectively (Figure 1).
3. With the identical value of the air excess coefficient, the O₂ content depends to a considerably lesser degree on the composition of the fuel than the CO₂ content.

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4. There are furnaces in which regulation of combustion on the basis of the carbon dioxide content is altogether impossible. These are cement and lime kilns, in which carbon dioxide produced by the dissociation of carbonates is added to the carbon dioxide of combustion. In these cases, analysis for oxygen nevertheless permits determination of the air excess.

The first automatic gas analyzers for oxygen were based on the measurement of the decrease in volume of the gas mixture being analyzed as a result of consumption of the oxygen through combustion of an excess of an auxiliary gas (usually hydrogen) or by absorption of oxygen with yellow phosphorus or liquid absorbents.

The gas analyzers which appeared subsequently were based on the measurement of heat conductivity. Since the values for heat conductivity of oxygen and of nitrogen are very close, direct measurement of the heat conductivity could not be carried out, but differential measurement had to be performed.

Two variations of this type of measurement are known.

In the first variation, an excess of hydrogen is added to the gas to be analyzed, and the hydrogen contents in front of and behind the furnace in which the oxygen is consumed are compared on the basis of heat conductivity.

In the second variation, the gas is admitted into a furnace filled with red-hot coke and the concentration of the gas is judged on the basis of the carbon dioxide formed.

Oxygen gas analyzers on the basis of heat conductivity enjoyed a certain degree of acceptance; however, they have a number of shortcomings which prevent the wider introduction of apparatus of this type.

A number of attempts were made to determine the oxygen content by electrochemical means. They were based on the measurement of the strength of the depolarization current of a galvanic element, in whose electrolyte a concentration of oxygen in equilibrium with that of the gas was established.

The thermochromic gas analyzers for oxygen are the most sensitive and are useful for measuring the smallest concentrations of oxygen in various gas mixtures. These apparatus are based on measurement of the heat effect produced by oxygen consumed at a catalyst in an excess of combustible gas. In gas analyzers of this type, the gas flows past the sensitive element of a differential thermometer heated to the temperature at which the catalytic reaction takes place.

The concentration of oxygen is determined on the basis of the difference in temperature between two sensitive elements which are either thermocouples or resistance thermometers. The theoretical temperature increase with a content of one percent O_2 is more than $160^\circ C$. This implies that, in principle, oxygen content can be determined with an accuracy of the order of 0.001 percent.

Thermochemical gas analyzers of three main types are applied:

1. With burning to completion on a platinum wire heated to the requisite temperature.
2. With the gradual introduction of the gas to be analyzed past two resistance thermometers or thermocouples one of which carries the catalyst. The measuring compartment of the gas analyzer is placed into a furnace heated to the temperature at which the catalytic reaction will proceed.

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3. The third type differs from the above in that one of the resistance thermometers or one of the thermocouples is placed into a layer of granulated catalyst. This allows the use of more active catalysts and, in a number of cases, operation without preheating.

Figure 2 shows the scheme of a gas analyzer of the first type.

The gas to be analyzed enters through two pressure regulators 1 and 2 and the throttle 3 into the evaporation chamber with the nozzle 4. Liquid fuel with a low boiling point enters the chamber and is vaporized by the gas to be analyzed. The gas-vapor mixture, containing an excess of fuel vapor with respect to the oxygen, strikes the incandescent platinum coil of the measuring chamber, where the oxygen is consumed by burning the fuel.

The speed of the liquid entering the evaporator is kept constant by keeping the pressure constant by means of a float regulator at level 6 in the chamber 7. The rate of flow of the liquid is set by the capillary coil 8.

The temperature in the block [body?] of the gas analyzer is kept constant. This eliminates the influence of viscosity on the rate of flow of the liquid fuel and of the gas being analyzed, as the viscosity changes with the temperature.

To protect the capillary coil from clogging, filter 9 is installed in the path of the liquid fuel in front of the chamber 7.

The device described is suitable for the determination of comparatively high concentrations of oxygen (normal range 0 - 10 percent). Its indications depend on the accuracy of apportioning the flow of the liquid fuel and the gas to be analyzed and on maintaining a constant ratio of the two rates of flow.

Gas analyzers of the second type have high sensitivity and operate with high accuracy. The normal range of the device whose gas flow scheme is shown in Figure 3 is 0 - 1 percent.

The gas to be analyzed enters through filter 1 and the flow rate regulator 2, consisting of three pressure regulators and three throttles, then runs through a control rheometer 3 into the furnace 4, where the measuring (I_1 and I_2) and the comparison chambers (S_1 and S_2) of the gas analyzer are located. If the gas to be analyzed does not contain any hydrogen, the latter is added from the cathode of the electrolyzer 5. When the supply of gas into the device is stopped, the supply circuit of the electrolyzer is automatically shut off by means of the membrane contact of the manometer 6.

Figure 4 shows the scheme of the feeder (datchik) of an oxygen gas analyzer of the third type. It is a glass Dewar flask containing an active catalyst, palladium or platinum-palladium, which is effective at room temperature.

For regulating the indication when the activity of the catalyst decreases, a secondary device is connected to the thermocouple through the voltage divider R_1 . The resistance R_2 serves to increase the measuring range. For this, the switch is set in position 2.

Thermochemical gas analyzers require exact maintenance of the constant rate of flow of the gas to be analyzed which runs through the device, protection of the catalyst from poisoning, and periodic inspection of its activity by means of a special electrolyzer for oxyhydrogen gas which supplies a definite quantity of oxygen to the device.

The magnetic methods of oxygen determination, developed recently, are of the greatest interest.

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Oxygen, as far as almost all its physical properties are concerned, is not distinguishable from the gases generally accompanying it, so that the direct use of physical methods to determine oxygen is impossible. However, oxygen is sharply distinguished from other gases by its magnetic susceptibility. If we disregard nitrogen oxide, oxygen is practically the only paramagnetic gas (cf. table).

Values of the Volumetric Magnetic Susceptibility of Gases

<u>Gas</u>	<u>Temperature in (°C)</u>	<u>Volumetric Magnetic Susceptibility</u> <u>($K_v \cdot 10^6$)</u>
Oxygen	20	+ 0.151
Nitrogen	16	+ 0.05
Nitrogen	20	- 0.00055
Hydrogen	20	- 0.0002
Helium	20	- 0.00085
Argon	20	- 0.0086
Carbon dioxide	20	- 0.00093
Chlorine	15	- 0.00187
Methane	20	- 0.00054
Ethylene	20	- 0.00054
Acetylene	11	- 0.00056

The devices based on direct utilization of the magnetic susceptibility of oxygen are magnetic torsion balances on which the oxygen concentration in the gas mixture between the pole shoes of a magnet is determined according to the displacement of a glass body located in the nonhomogeneous portion of the field of a constant magnet.

This type of device has found use only for purposes of laboratory investigations.

In all the rest of the work on magnetic determination of oxygen, a number of secondary phenomena connected with the paramagnetism of oxygen were utilized.

In the 1930's, the so-called Senftleben effect was discovered, which established the effect of a magnetic field on the heat conductivity of paramagnetic gases.

In 1939, it was proposed in Germany to utilize the Senftleben effect for the determination of oxygen in pressurized cabins of high-altitude aircraft. The design proposed for this purpose is a gas analyzer based on the measurement of heat conductivity. It has two chambers filled with the gas to be analyzed. One of the chambers is in the homogeneous magnetic field, the other outside the field. A decrease of heat conductivity in the magnetic field was observed. This change is proportional to the oxygen content of the air being analyzed.

As a result of experimental work carried out in 1940-1941, about 15 patent applications connected with the magnetic determination of oxygen were filed in Germany.

Most of these patents must be regarded as so-called "protective" patents which were taken out not for practical application of the device, but to prevent competitors' designs from appearing on the market.

The Senftleben effect was not utilized in any of the subsequent work, since devices built on the basis of this principle have extremely low sensitivity. For instance, in the case of air a one-percent change in heat conductivity is reached with a magnetic field of 30,000 Oersted.

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In all the other investigations and devices for automatic determination of oxygen, a phenomenon was utilized which was discovered and investigated by Faraday, the so-called magnetic wind or thermomagnetic convection, which originates in a nonhomogeneous portion of the magnetic field in the presence of a temperature gradient in the paramagnetic gas.

Faraday observed that the flame of a wax candle changed its shape in an electromagnetic field, as though it were under the effect of wind which was blowing it out of the magnetic field.

We reproduced this observation and photographed both positions of the flame on one picture (Figure 5). The current in the circuit of the electromagnet was shut off after half the exposure time had elapsed, so that both positions of the flame are shown in the picture.

The thermomagnetic convection, in substance, consists of the fact that the magnetic susceptibility of oxygen decreases with increasing temperature, i.e., the mixture virtually becomes less paramagnetic. Thus, if the temperature of a paramagnetic gas rises in a section with increasing magnetic field strength, the cold gas will be sucked into the magnetic field. The intensity of the thermomagnetic convection is proportional to the partial pressure of oxygen.

In automatic magnetic gas analyzers, the cooling effect of this convection current is exerted on the heating element which increases the temperature of the gas. In the original German devices of this type, a fine incandescent platinum filament was located in the nonhomogeneous section of the magnetic field (Figure 6). The reference section of the bridge -- a second filament of the same kind -- was placed outside the field. The cooling of the filament located in the magnetic field depended on the combined effect of the magnetic field and the field of gravity causing heat convection.

To prevent displacement of the conducting filament in the magnetic field, the circuit was supplied with alternating current, and the unbalance of the bridge transmitted to a tube amplifier. After the war, this design was copied by the Americans, who built a gas analyzer to investigate the composition of exhaled air in pressure chamber tests.

However, this type of device was not widely accepted because of its complex design, the necessity of using an amplifier, and the dependence of the indication on the heat conductivity of the gas mixture.

Later American models use rigid heating elements in the form of platinum coils mounted on fine porcelain stems (Figure 7). This permits the use of a dc bridge circuit and eliminates the need for an amplifier. The use of an electric barometric pressure compensator in these devices is noteworthy.

In Germany, work on magnetic gas analyzers was carried out also by the I. G. Farbenindustrie, but was interrupted at the time of the war while still in the experimental stage.

These devices have no comparison chambers and thermomagnetic convection is measured in a strictly horizontal direction, so that the influence of the gravity field is eliminated.

In the gas analyzer developed in our laboratory, the feeder of the device (Figure 8) is an annular chamber with a horizontal connecting tube. The gas enters the chamber from the bottom and goes out through the top. A heating coil is mounted on the tube, and the pole shoes of a permanent magnet are located at the edges of the coil.

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To one side of the axis of symmetry of the magnetic field there is colder, and thus more highly paramagnetic air. Due to this fact, there is a pressure drop in the horizontal tube, causing a motion of gas in such a manner that the rate of flow of the gas is proportional to the concentration of oxygen.

The heating coil is divided into two parts and serves as a thermoanemometer measuring the rate of flow.

The section of the coil through which the gas passes first is cooled; the second section is heated by the flow of the gas. The sections of the coil are compensated or noncompensated arms of a bridge, and the temperature difference in the sections is recorded on an automatic registering device.

The gas analyzer has satisfactory sensitivity and has an error of 60 to 100 mv with 100 percent oxygen. Its scale comprises 0-10 percent. The heat conductivity of the ballast gases with which the oxygen is mixed has no effect on the indication of the device. Nevertheless, the indication depends on the viscosity and heat capacity of the mixture. The viscosity determines the rate of laminar flow of the gas in the tube, and the heat capacity determines the quantity of heat taken away by the gas from the thermoanemometric tube. In most cases of analysis for oxygen, this is of no essential importance.

Automatic Analysis of Mixtures of Organic Gases and Vapors

In connection with the development of the oil-refining industry and of heavy organic synthetic industry in general, there arose the problem of determining organic gases and vapors in complex gas mixtures. The components of these mixtures, in a number of cases, are similar in their chemical and physical properties.

A separate determination of some of the components is usually required, but in some cases, such as in the determination of the characteristics of narrow fractions produced in one way or another, it is sufficient to determine the average molecular weight of the gas which is characterized by its density. The density of the gas mixture can serve as a measure of the concentration of the component being analyzed, even in those cases where its density differs considerably from that of the other components.

It is interesting to note that the German chemical industry distributed until recently, a cumbersome cyclically acting device of the Badische Anilin- und Sodafabrik, based on the effusion principle. This device is still being used.

Several firms developed a device for measuring the density of the gas to be controlled by comparing it with that of a reference gas. This measurement is based on the determination of the pressure drop in front of diaphragms, the gases being supplied by two centrifugal blowers which are mounted on a common shaft (Figure 9). This device represents a modification of the old Ranerex gas analyzer.

The Ranerex gas analyzer, which can by no means be considered a device of high accuracy, has been copied and is now being produced by American firms.

Among German devices, the Pollux gas analyzer, constructed on the principle of the gas balance, is of interest. This gas analyzer was produced before the war. It is a gas balance made of glass, with automatic temperature and pressure compensation, and with technical registration of the balance beam deflection. The balance beam is connected through a magnetic clutch with the writing mechanism (Figure 10). The accuracy of the device is ± 1 percent of the maximum deflection on the scale.

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The Pollux gas analyzer is suitable only for work with dust-free and dry gases.

It should be pointed out that gas balances with automatic temperature and pressure compensation were developed in the Soviet Union nearly 20 years ago. [2]

Among the devices of the laboratory type, the gas balance with electromagnetic compensation (Figure 11) is notable.

In this device, two quartz floats 1 and 2 of different volume are counterpoised on the beam of a rigid balance system. Float 1 is a complete sphere with an enclosed gas volume, float 2 is a cylindrical body with an opening. The surfaces of the floats adjoining the gas to be analyzed are made uniform to eliminate the effect of the weight of the adsorbed gas.

The balance system is located in a glass chamber 3 and is initially balanced in a medium of standard gas at the proper pressure and temperature. Upon subsequent filling of the chamber with the gas to be analyzed, a position of equilibrium is established by means of electromagnet 4 which is adjusted manually by varying the strength of the current in its line. The difference in density of the gas under investigation and the gas being analyzed is characterized by the strength of the current in the line of the electromagnet when the balance is in equilibrium. The moment of equilibrium is observed by an optical apparatus 5 which allows viewing the mirror image of the balance beam indicator and of a stationary dial. The sensitivity of the device reaches 50 to 100 milligrams per cubic meter, i.e., 0.005 to 0.01 percent.

We must touch briefly on the automatic gas density measuring device developed in our laboratory. This device is based on the hydrostatic principle (Figure 12). The columns of the controlled and the standard gas, which are not very high (200-250 mm), are brought to the same density by establishing the temperature difference required for this purpose. Balancing is achieved by shutting off the flow of gas in the connecting tube which contains a sensitive zero anemometer that detects gas flow rates of the order of 0.1 ml per minute and distinguishes the direction of the flow. The device operates automatically, and has an automatic recording device or an electric indicator. The measuring error is about 0.1 percent. The device measures density reduced to normal temperature and pressure.

Turning to the question of selective determination of individual components of multicomponent organic gas mixtures, it should be pointed out that this is a complex problem, particularly when continuous automatic analysis of mixtures is considered.

The problem is made somewhat easier in cases where a component or a group of components, sharply distinguished in their chemical or physical properties from the ballast gas, is to be determined. This takes place, for instance, in the determination of benzene and its homologues in coke oven gas, or in the determination of the total amount of unsaturated hydrocarbons in petroleum pyrolysis gases.

Volumetric gas analyzers have been used only in the latter case for the purpose of automatic control. But, on the whole, these devices could not be used in organic gas analysis.

This also applies to the direct application of gas analyzers based on the measurement of heat conductivity.

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A very promising procedure for the analysis of organic gases is the sorption method.

An automatic gas analyzer for the determination of benzene in coke gas, based on the recording of the weight increase of a container filled with activated carbon (Figure 13), has been used for some time in Germany, but has not caught on. The weight increase of the carbon is compensated by the movement of a little chain. The movement is produced by a weight upon closing of a relay activated by the contact of the pointer of the scale. The chain is kinematically connected with the pen of the recording device. At definite intervals the pen is returned to the zero position, whereupon the equilibrium position of the balance is automatically re-established by means of second chain. The peaks of the saw-tooth diagram, as obtained in such a system of recording, are a measure of the concentration.

In 1939-1941, N. A. Figurovskiy and the author established in principle the possibility of determining vapors of organic substances in gases by direct measurement of the electric resistance of thin layers of activated carbon applied to a dielectric.

This effect reaches very high dimensions; for instance, in saturated benzene vapor the resistance of the activated carbon layer is decreased five to seven times. The resistance measurement is reversible and is carried out with comparatively low inertia.

We conducted experiments with continuous recording of the content of various organic vapors by this method.

Apparently, adsorbents will also find use in separate determination in gas analyzers based on various physical and physicochemical methods.

The very promising method of fractionated desorption (chromatographic) is used for intermittent analysis of multicomponent mixtures. The method is based on the successive replacement of the separate components of a gas mixture, adsorbed in a long tube filled with a sorbent, by a flow of pure air or of air containing a substance with higher adsorption ability than the components of the gas.

Thus, air which was passed through the sorbent-filled tube will contain practically only one component of the mixture to be analyzed. For its analysis, the heat conductivity can be measured, as was done in the work cited above. [4]

Turning to optical methods of analysis, we must touch on the use of the infrared spectra. The basic feature of these spectra is that they characterize the molecular structure.

The oscillations of separate atom groups in a complex molecule take place independently, to a large degree, and definite groups have characteristic frequencies of oscillation.

Optical infrared methods may be subdivided into methods with and methods without spectral dispersion.

Industrial devices using spectral dispersion have been developed by Americans. These devices measure the amount of absorption over a narrow range of long waves which corresponds to the specific maximum of absorption for the given substance. The devices with spectral dispersion are of complex design and cannot be considered promising for wide use on an industrial scale.

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Of greatest interest are devices for selective analysis of gases without spectral dispersion. These methods were first developed in the USSR by M. L. Veyngerov. [5]

The URAS gas analyzer is of technical interest. It is produced in Germany and is built according to the principles developed by Veyngerov.

The device operates as follows. (Figures 14 and 15): Two beams of infrared radiation from an emitter 1 pass through the "obturator" / shutter 2 rotatable by motor 3 at a frequency of 6.5 periods, and are then directed through two containers 4 and 5. One of these containers is filled with dry CO₂-free air, and the gas to be analyzed is run through the other container. The beams of radiation energy further enter the radiation receiver chambers 6, which are filled with air containing the component to be analyzed.

The radiation receiver chambers are connected to the housing of the membrane condenser 7.

When the component to be analyzed appears in the gas, the intensity of the radiation beam which has entered the measuring chamber of the radiation receiver decreases. As a consequence, a variable component whose magnitude depends on the concentration of the gas component to be analyzed is superimposed on the constant pressure difference. The constant pressure difference depends on the temperature difference between the chambers in the nonirradiated state. The membrane condenser receives the variations in pressure drop as variations in capacitance. These variations, after amplifying, are transmitted to the automatic recording device.

The sensitivity of the device is sufficiently high. For instance, devices have been produced whose entire scale comprises 0.05 percent CO₂ or CO. Selectivity of the determination is achieved because energy in the radiation receiver chambers is taken up by the component being analyzed, so that a decrease in radiation at frequencies which correspond to the absorption region of the given substance is measured. Full selectivity of the analysis is obtained only in those cases where the absorption curves of the component being analyzed and of the ballast gas do not overlap in the infrared region. With partially coincident absorption curves, an error is introduced into the measurement. It is characterized by the interference coefficient

$$\epsilon_{2:1} = A_2 C_1 / A_1 C_2$$

where C_1 is the concentration of the component to be analyzed, C_2 the concentration of the interfering component in the ballast gas, and A_1 and A_2 are the respective errors on the secondary device.

The magnitude of the interference coefficient depends on how close the substances are in their composition and structure. For instance, $\epsilon_{CO:CO_2}$ is approximately 0.001, which means that at equal concentrations of CO and CO₂ the measurement error is 0.1 percent.

This error is much greater for substances which have, to a large degree, superimposing spectra, as in the case of homologues of saturated hydrocarbons. In such cases, a gas color filter is installed in front of the containers; this retains the frequency of the radiation of the impurity that causes the error.

The basic shortcoming of this gas analyzer is the complicated amplifier circuit which contains tube electrometers. The necessity for using it is due to the operation at low frequencies.

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Recently, a modification of the URAS gas analyzer has been developed which determines three components of a gas mixture. In this device, the radiation receiver chambers are filled with a mixture of three components to be analyzed, and six gas color filters are placed on the rotating disk. Each filter contains two components.

One of the most thorough methods of complete analysis of multicomponent mixtures is the mass spectrometer method. As distinguished from the mass spectrograph which records the effect of ion beams on a photographic plate, the mass spectrometers are based on the continuous measurement of ionic currents.

Washburn's analytical mass spectrometer is designed for the analysis of separate gas samples. In this device, the gas to be analyzed is drawn into the ionization chamber, where the molecules form ions in the space behind the cathode. The ions are then subjected to the action of an electric and magnetic field and move on a curved trajectory. The radius of the trajectory depends on the ratio between the field, the mass of the ion, and the number of its charges. By evenly modifying the electric or magnetic field, it is possible to pass in turn ions with a definite mass-charge ratio through the slit located on the trajectory of the bundle of ions separated according to mass and charge. The ions are discharged on the collector. The ionization current is amplified and recorded on an automatic registration device. The recording device draws four curves simultaneously, which differ according to the scale of sensitivity. This permits determination with satisfactory accuracy of components contained in the gas in small concentrations, together with determination of components present in high concentrations.

The analytical mass spectrometer permits making a complete analysis of a mixture with ten components within half an hour. The volume of gas required for one analysis is 0.1 ml.

The mass spectrometers in existence, despite all the qualities mentioned above, have serious shortcomings. For instance, in addition to the half-hour duration of the analysis, it takes about 2 hours to decipher the mass spectrogram. The mass spectrometer is a complicated and cumbersome device and takes up a lot of room. At present, the multicomponent mass spectrometer is not yet a device for the continuous automatic analysis of gases on an industrial scale.

Determination of Combustible Gases in Air

This problem is very important in the development of the technological utilization of gaseous fuel, and also in petroleum, coal, and chemical industry.

For control to prevent the danger of explosions, portable gas analyzers, stationary indicating, or automatic recording devices and, finally, simple signal devices are used, depending on local working conditions.

In connection with the possibility of local accumulation of combustible gases or vapors, it is sometimes expedient to use automatic gas switches (gazoviy pereklyuchatel') in the installation of stationary devices.

A great number of various designs of devices for controlling combustible gases in the air have been developed.

Mention must be made of diffusion gas analyzers, based on the difference in penetration speed of gases with different densities through porous diaphragms. The diffusion gas analyzers which have been in use until now (diffusion gas analyzers have been known for a long time; the first test of their practical use was conducted at the time of World War I for the indication of chlorine) are closed chambers with a diffusion diaphragm and a pressure gauge (figure 16).

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Upon appearance in the air of gaseous admixtures with low density and consequently with a high diffusion rate, the process of equalization of the partial pressures of the components of the gas mixture does not take place uniformly. Thus, the excess pressure in the chamber grows at first, reaching a maximum within a certain time, and then the pressure is again equalized. With the appearance of heavy gases in the air, an analogous process produces rarefaction in the chamber.

Recently, several modifications of the portable diffusion gas analyzer have been released and widely advertised abroad. However, they have found only limited use. This is due mostly to the fact that the analysis is not sufficiently specific, and also to a number of operational drawbacks in the use of the devices. But all the diffusion methods of analysis are distinguished by simple, explosion-proof designs and afford the possibility of building devices which do not measure the absolute value of the content of admixtures in the air, but the rate of increase of their concentration. This might be of practical significance in some cases.

Among the devices based on optical methods of determining combustible gases, there is a portable interferometer for determining methane in coal mines. The device was in use in Germany and in Japan. Its deficiencies are its comparatively large dimensions and the necessity of a visual compensation attachment. If carbon dioxide is present in the air, the air must be passed through an alkali filter. The sensitivity of the portable interferometers is not high. Their scale comprises 0 - 100 percent methane, graduated in one percent. The gas interferometers are not suitable for the determination of mixed gases of varying composition.

The gas analyzers described above, based on the absorption of infrared radiation, have been used for continuous automatic control of the content of combustible gases and vapors. They have been used in combination with automatic gas switches, which permit drawing samples of air into the device from various points in the space being controlled.

The most expedient method of analysis of combustible gases in the air is the determination of the heat effect. The heat of combustion is a very specific property of all combustible gases and allows building of single-type devices for various purposes.

Two devices based on this method were developed in our laboratory. They are a portable gas analyzer and a signaling device for combustible gases. In the portable gas analyzer, as distinguished from other analogous devices, the gas is not drawn into the device during the analysis, but a gas sample, enclosed in a chamber, is analyzed and the maximum deflection of the galvanometer pointer at the moment of switching on of the instrument is observed. This establishes a number of operational advantages: the danger of explosion is decreased, a subsequent analysis of the sample taken is possible, the duration of the analysis is cut to 1-2 seconds, and the consumption of energy for supplying the device is reduced. The electrical circuit of the device is an unbalanced Wheatstone bridge. The scheme of the gas flow is shown in Figure 17.

The device has a range selector switch for three scales. It permits separate determination of CH_4 and of $\text{CO} + \text{H}_2\text{O}$ by means of different filaments, and also the determination of heavy hydrocarbons by means of an active carbon filter.

The device has been tested under various operation conditions.

The signaling device for combustible gases in the air is also based on measurement of the heat effect of combustion (Figure 18). The platinum coils 1 of the measuring and comparison chambers of the gas analyzer are located inside the thermocylinders 2 of the differential manometric thermometer. If there is a combustible gas in the air, the incandescence of the coil in the measuring chamber increases,

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and thus a temperature difference in the thermocylinders is created. The pressure drop created thereby is transmitted to the membrane of the differential manometer 3 and then to the pointer of the indicator with luminous reading, which is kinematically connected to the membrane. The membrane also closes the contact device 5, if a dangerous concentration of gas is reached. When the gas concentration becomes dangerous, the signal lamp 6 is turned on.

We have discussed the methods and apparatus used for solving only a few of the problems of gas analysis. The volume of problems facing industry is much greater. The complexity of the problem of gas analysis in industry is due to the fact that a great number of gases which differ in chemical and physical properties are dealt with and that the procedures in question are based on a great number of chemical, physicochemical, and physical methods.

An attempt can be made to systematize the basic methods of gas analysis used at the present:

1. Volumetric methods, based on the measurement of the decrease in volume of the component being analyzed
2. Manometric methods, based on the measurement of the rarefaction of the component being analyzed due to its reaction
3. Thermochemical methods, based on the measurement of the heat effect of chemical reactions
4. Methods based on measurement of the heat conductivity of the gas mixture
5. Methods based on the measurement of density
6. Optical methods, based on measurement of the optical properties of the gases themselves or of absorbent solutions
7. Electrochemical methods, based on the determination of electric conductivity (conductometric), the potential difference (potentiometric), and the current (amperometric) in absorbent solutions
8. Sorption methods, based on the adsorption or desorption of the gas mixture component being analyzed
9. Magnetic methods
10. Mass-spectrometric methods.

Of the ten methods enumerated here, the last eight can definitely be considered as promising for practical application in industry.

It follows from this that the number of designs of gas analyzers must be comparatively large.

Although the variety of methods makes the development of devices difficult, the multiplicity of designs might [otherwise?] create serious obstacles in the industrial production of gas analyzers. We therefore consider it absolutely necessary to effect a transition to standard blocks and parts for utilization in automatic gas analyzers. Even in gas analyzers which are very different in the principle of their operation, a considerable number of unit-type elements could be used.

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This kind of standardization will make it possible for industry to deal with a limited number of additional blocks and parts in perfecting the gas analysis apparatus now being put out or in changing to new designs.

The large-scale development of research and design work in gas analysis, and, especially, the considerable expansion of the output of gas analyzers with modern technical features should provide for the growing needs of our industry.

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[Appended figures follow.]

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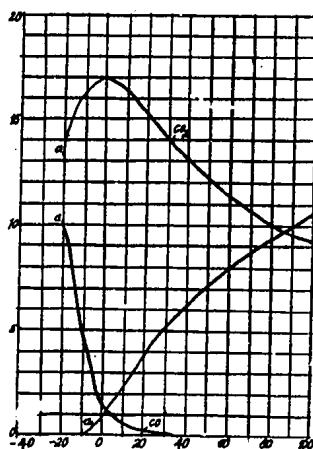


Figure 1. Graph of the Dependence of the Concentrations of CO_2 , CO , and O_2 on Excess Air
Ordinate: Excess Air, in %
Abscissa: Concentration of Gas, in %

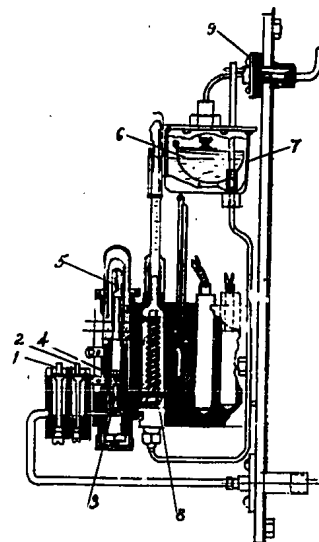


Figure 2. O_2 -Gas Analyzer With Combustion on Filament

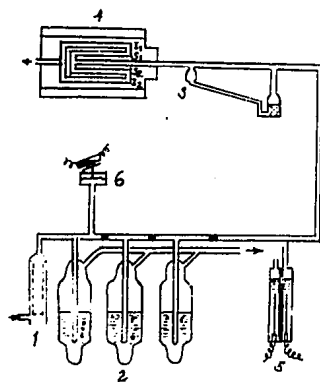


Figure 3. Scheme of Gas Flow of O_2 Analyzer

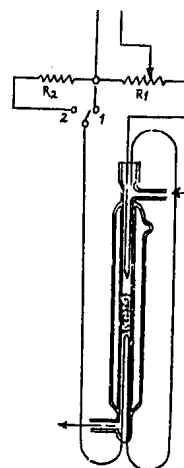


Figure 4. Feeder (datchik) of Gas Analyzer With Bulk Catalyst

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Figure 5. The Effect of Magnetic Wind on a Candle Flame

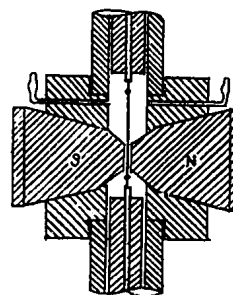


Figure 6. Fundamental Scheme of Magnetic Gas Analyzer With Heating Filament

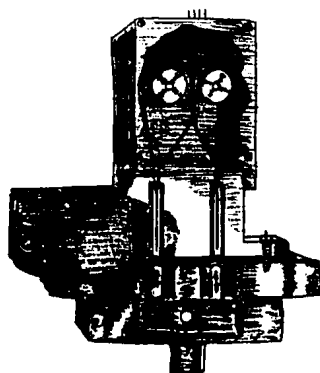


Figure 7. Scheme of Magnetic Gas Analyzer With Rigid Heating Elements

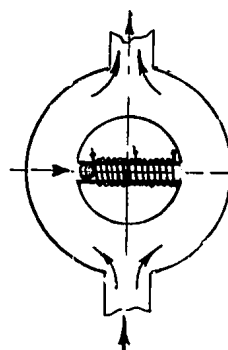


Figure 8. Scheme of the Annular Feeder of a Magnetic Gas Analyzer

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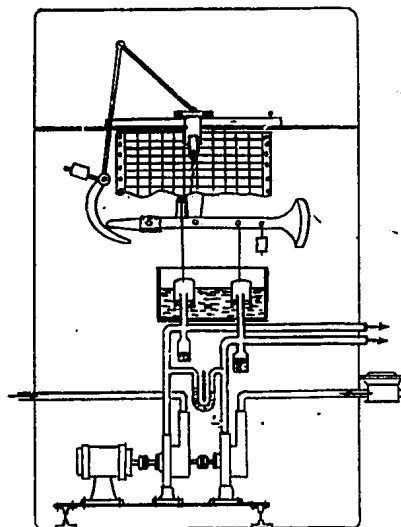


Figure 9. Scheme of Density Measuring Device

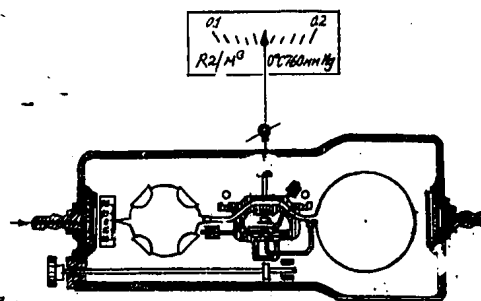


Figure 10. Scheme of the Pollux Gas Analyzer

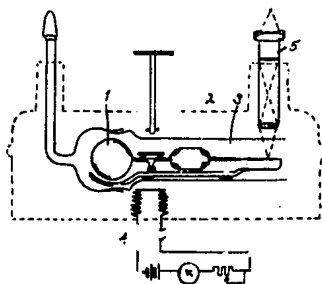


Figure 11. Scheme of Gas Balance With Electromagnetic Compensator

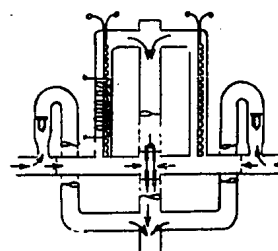


Figure 12. Scheme of Compensation Measuring Device of Gas Density

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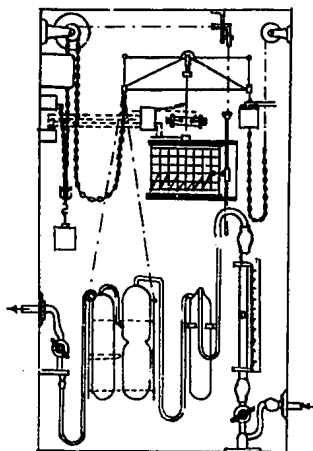


Figure 13. Scheme of the Adsorption Balance Gas Analyzer

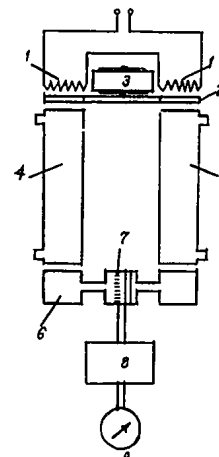


Figure 14. Scheme of the URAS Gas Analyzer

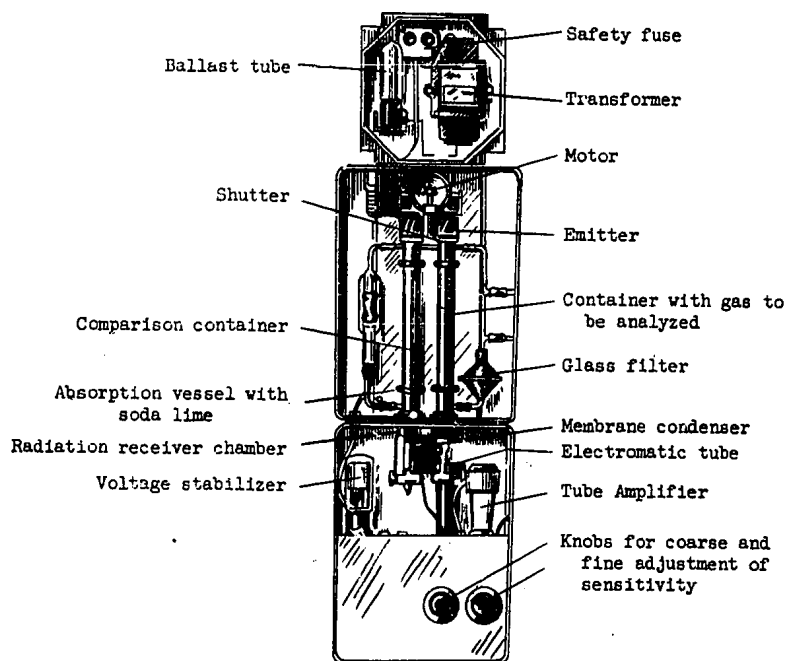


Figure 15. Exterior View of the URAS Gas Analyzer

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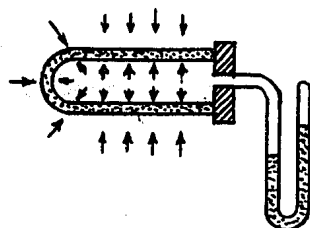


Figure 16. Fundamental Scheme of
Diffusion Gas Analyzer

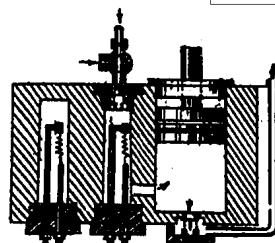


Figure 17. Scheme of Gas Flow in
Portable Gas Analyzer for Com-
bustible Gases in Air

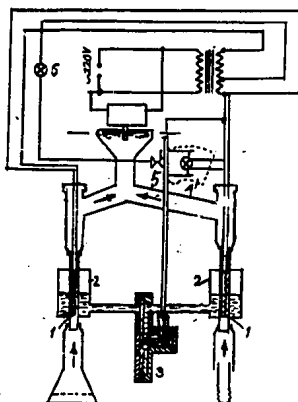


Figure 18. Scheme of Signal
Device for Combustible Gases
in Air

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